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Diode Laser Spectra of CCl_2F_2 Near $10.8 \mu\text{m}$: Air-Broadening Effects

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DIODE LASER SPECTRA OF CCl_2F_2
NEAR $10.8\mu\text{m}$; AIR-BROADENING EFFECTS

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ABSTRACT

Laboratory spectra of CCl_2F_2 in the $10.8\mu\text{m}$ region has been recorded using a tuneable diode laser spectrometer. Effects of air-broadening at pressures up to 48 Torr show that spectral structure should be exhibited under high resolution at altitudes as low as 19 Km. The single-line pressure-broadening coefficient for CCl_2F_2 is estimated to be 8 MHz/Torr FWHM.

Stratospheric dichlorodifluoromethane is of increasing interest because of its possible role in the ozone-depletion chemistry of the upper atmosphere (Clyne, 1974; Molina and Rowland, 1974; Cicerone et al. 1974). It is important in this context to have a knowledge of the altitude profile of the CCl_2F_2 mixing ratio, and this can be obtained experimentally either from insitu measurements (Schmeltekopf et al. 1976) or from inversion of high-resolution atmospheric spectra. The second technique lends itself well to ground-based monitoring, but requires some knowledge of the behavior of the spectra under conditions of pressure and temperature similar to those in the stratosphere. Recently, CCl_2F_2 has been detected in solar absorption with balloon-borne (Williams et al., 1976) and ground-based (Bradford et al., 1976) spectrometers. Goldman et al., (1976) have reported laboratory spectra of the $10.8\mu\text{m}$ band of CCl_2F_2 obtained at moderate resolution (0.06 cm^{-1}).

With the introduction of infrared laser heterodyning as a remote sensing technique (see, for example, McElroy, 1972, Peyton et al., 1977, and Mumma et al., 1977), it has become possible to obtain ultra-high resolution (10^{-4} cm^{-1}) atmospheric spectra. Carbon dioxide lasers used as local oscillators provide coverage of several discrete segments, each about 0.1 cm^{-1} wide, in the $10.8\mu\text{m}$ band of CCl_2F_2 . Tunable diode lasers, which are available with output powers approaching the required level for shot-noise limited heterodyning (Mumma et al., 1975a and b, Ku and Spears, 1977), provide coverage at any wavelength

in this region in segments up to several wavenumbers wide.

In anticipation of the need for ultra-high resolution laboratory data in the interpretation of stratospheric spectra, a tunable diode laser spectrometer has been used to record the regions near 922.8 cm^{-1} and 921.7 cm^{-1} in the vibration-rotation spectrum of CCl_2F_2 . These are the strongest absorption regions in the $10.8\mu\text{m}$ band, and correspond to the Q-branches of ν_6 (Flyler and Benedict, 1951) for the $\text{C}^{35}\text{Cl}_2\text{F}_2$ and $\text{C}^{35}\text{Cl}^{37}\text{ClF}_2$ isotopic species, respectively.

The sample was taken from a standard commercial cylinder and was not isotopically purified. A pressure of 0.200 Torr CCl_2F_2 was placed in a 30 cm length cell at ambient temperature (25°C) and air was introduced into the cell to achieve the desired partial pressures. Gas pressure in the sample cell was measured with a 0-1000 Torr MKS type 170 Baratron pressure meter. Wavenumber calibration of the spectra was established using a germanium Fabry-Perot etalon and NH_3 lines of known frequency.

The effects of air-broadening on the 922.8 cm^{-1} spectra are shown in Figure 1. In this region, as in all portions of the ν_6 band, the line density is so great that single-line analysis is impossible. The structure exhibits good intensity contrast, however, at pressures corresponding to altitudes in the upper atmosphere.

In particular, this is true of the 922.9 to 922.7 cm^{-1} portion of the spectra, where the absorption features (which are each due to more than one transition) are especially prominent and regularly spaced. This spacing, 0.014 cm^{-1} (408 MHz), is wide enough to retain spectral structure at atmospheric pressures as high as 48 Torr, or

altitudes as low as 19 Km. The apparent broadening in this region, as measured from the full width at the absorption level halfway between minimum and maximum absorption for each feature, is 2 MHz/Torr. The single-line broadening coefficient for CCl_2F_2 can be estimated from this spectra to be $\Delta\nu = 8 \text{ MHz/Torr FWHM}$.

It should be noted, for the purpose of heterodyne monitoring using a CO_2 laser local oscillator, that the P(42) transition of the $10.4\mu\text{m}$ lasing band of $^{12}\text{C } ^{16}\text{O}_2$ occurs near this region at 922.9143 cm^{-1} . Also, the R(12) line of $^{13}\text{C } ^{16}\text{O}_2$ occurs at 923.1114 cm^{-1} , near the branch head.

The structure near the branch head (923.2 cm^{-1}) is the most recognizable series anywhere in the spectrum. A second Q-branch head, probably corresponding to the $\nu_6 + \nu_2 - \nu_2$ hot band (Goldman et al. 1976) appears at 922.7 cm^{-1} . A more complete analysis of the ν_6 band will be the subject of a later paper.

The air-broadening effects in the 921.7 cm^{-1} region are shown in Figure 2. Although some high-resolution structure is discernible at pressures as high as 24 Torr (altitudes as low as 23 km), the intensity contrast here is not as pronounced as in the 922.8 cm^{-1} region and is not expected to be as useful in the analysis of stratospheric spectra.

The CO_2 laser heterodyne spectrometer which is coupled to the 48-inch telescope at the Goddard Space Flight Center (Mumma et al., 1977) has been used to record ground-based solar absorption spectra of the $10.8 \mu\text{m}$ band of CCl_2F_2 , and the work reported here was instigated

as part of that program. The heterodyne observations are presently being completed in that region, and results will be reported later.

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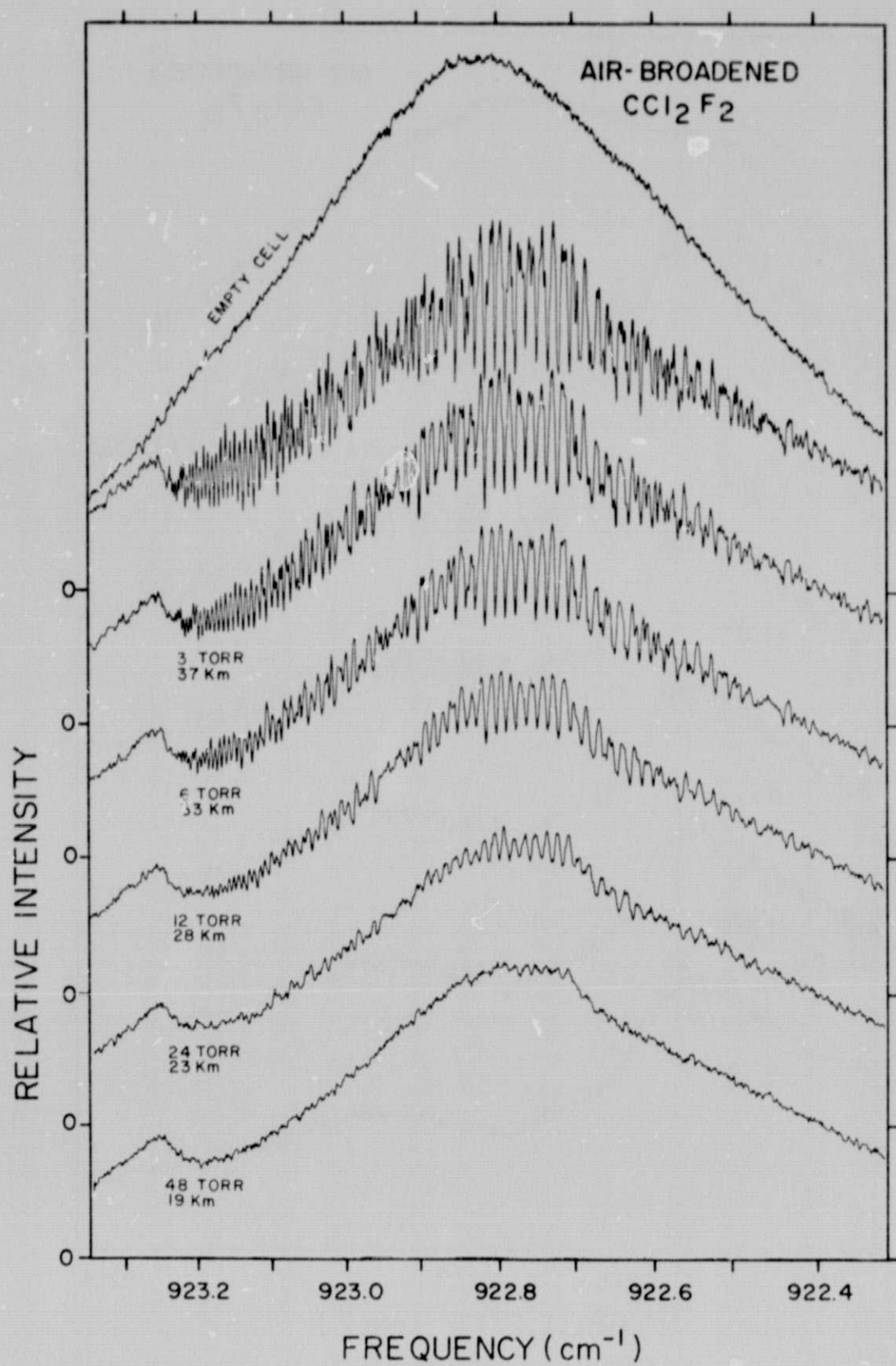
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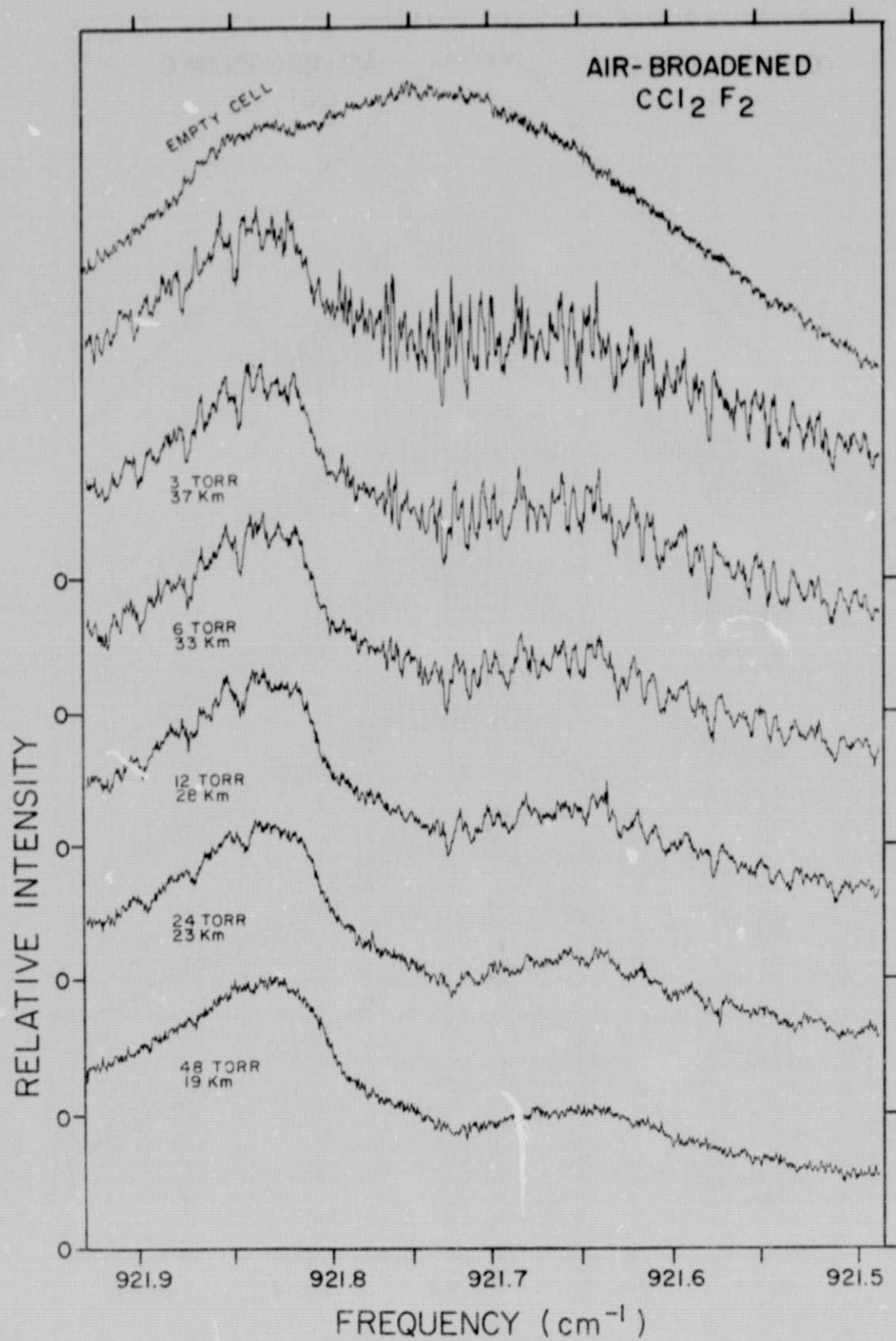
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FIGURE CAPTIONS

- Fig. 1 Laboratory air-broadened spectra of CCl_2F_2 near 922.8 cm^{-1} .
The 30 cm sample cell was filled to 0.200 Torr CCl_2F_2 (top trace) and air was then introduced to reach the partial pressures indicated. Temperature = 25°C . Altitudes are according to U.S. Standard Atmosphere, 1976. Note that the ordinate is linear in diode current and therefore slightly non-linear in frequency.
- Fig. 2 Laboratory air-broadened spectra of CCl_2F_2 near 921.7 cm^{-1} .
Remarks in the caption to Figure 1 apply here also. Note that the range of the frequency scale is less than in Figure 1.





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